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SEMICONDUCTOR ALLOYS(U) ILLINOIS UNIV AT URBANA DEPT OF  
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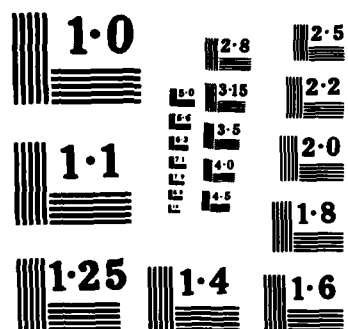
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Final report on the Office of Naval Research Contract

by John D. Dow, Principal Investigator

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The principal investigator has completed a sizeable research program studying superlattices, impurities in semiconductors, surface and interface states, Schottky barriers, many-body effects in x-ray and Auger spectra of metals, and the physics of semiconductive alloys. Here we list a few of the recent results *pertaining to*

A. Substitutional point defects

Recently Hjalmarson et al., of our group, have presented a theory of the major chemical trends in the energies of substitutional,  $sp^3$ -bonded deep impurity levels in zincblende hosts [75]. This work provided a successful theoretical explanation of data for the isoelectronic N trap in  $GaAs_{1-x}P_x$  [67]. More recent work by Hjalmarson shows that his model predicts the major chemical trends for deep traps in all the well-studied zincblende hosts. There are, of course, corrections to the Hjalmarson model due to lattice relaxation and to charge-state splittings; these can be significant. But if one accepts the initial simple version of the model in the context of its purpose, namely to predict chemical trends and to indicate which impurities are likely to produce deep levels or shallow levels, then it has been quite successful. (Lattice relaxation and charge-state splittings have been added to the model successfully in unpublished work by Sankey et al. of our group.) The extensive literature of deep levels has been reviewed in Hjalmarson's thesis, and recent work, with many approaches complementary to our own, has been cited extensively in the publications cited at the end of this proposal. Here we cite only the literature produced by our group.

The central qualitative idea of the Hjalmarson model is that the deep impurity levels within the fundamental bandgap are orthogonal to impurity-like hyperdeep levels, and hence are host-like. (For O or N in GaP, the hyperdeep levels lie within or below the valence band.) Confirmation of the hyperdeep level idea is contained implicitly in the recent magnetic resonance data for Si:N by Brower. The original Hjalmarson theory is limited, however, in that it treats only substitutional,  $sp^3$ -bonded point defects. (Very recently Vogl, a former member of our group, has extended the theory to substitutional transition metal impurities in III-V semiconductors.)

The Hjalmarson theory reproduces the charge densities measured by electron spin resonance and electron nuclear double resonance for the defects  $S^+$  in Si (Fig. 2) and the electron spin resonance spectra of  $Se^+$  and  $Te^+$  in Si, indicating that it is as accurate a theory as exists for these deep levels [108][138].

B. Laser degradation

We have proposed a mechanism of III-V rapid laser degradation (Fig. 3) and a means of inhibiting the mechanism [127]. We have proposed that dangling bonds form self-reproducing non-radiative killer centers that assist the growth of dislocations. The degradation mechanism can be inhibited by

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selecting a material whose dangling bond deep levels lie outside the band gap. In-rich quaternary alloys have this property (and also do not exhibit rapid degradation, as Ga-rich alloys do). We have calculated the phase diagram for rapid degradation. Experimental support for these ideas has recently been obtained by Ueda et al. of Fujitsu. We have also proposed that gradual degradation is assisted by antisite defects, and have predicted a corresponding phase diagram for that process.

#### C. Central-cell scattering effects on mobility

We have shown that the central-cell potential of a defect can have a significant and even dominant effect on the scattering of carriers, under certain conditions [132]. Thus there are conditions under which Coulomb scattering by defects is not the dominant scattering mechanism, and the central-cell scattering limits the mobility.

#### D. Pressure dependence of deep levels

We have predicted the pressure dependences of deep levels in GaAs and explained why deep levels are so insensitive to pressure, relative to shallow levels [120]. (The shallow levels are "attached" to band edges which depend on the nearest-neighbor overlap integrals — and these integrals change rapidly with pressure. Deep levels are sensitive to changes of only the average conduction band and valence band energies — which do not change much with pressure.) Based on these predictions and existing data, we have narrowed the candidates for the famous EL2 defect down to two: an antisite defect or oxygen (or complexes involving these defects). The latest experimental word from the last Lund conference is that both defects appear to be present in the line identified as EL2.

#### E. Deep levels in quaternary III-V alloys

We have predicted the contours of constant deep level energy as functions of alloy compositions  $x$  and  $y$  for deep vacancy and antisite defect levels in quaternary alloys such as  $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{P}_x$  [103][133][134].

#### F. Deep levels in $\text{Si}_x\text{Ge}_{1-x}$ alloys

We have predicted the chemical trends of deep levels in these interesting Group IV alloys. A notable prediction is that the normal shallow dopants P and As produce deep levels near the conduction band crossover,  $x=0.2$  [135]. Experimental evidence supporting this prediction has been provided by recent Si 2p core exciton synchrotron radiation measurements of B. Bunker et al..

#### G. Deep levels in CuCl

Numerous speculations concerning the nature of electronic states in CuCl have been made during recent years. We have contributed to the elucidation of the electronic properties of this interesting material by predicting successfully the nature of the deep level spectra for numerous impurities [102].

## H. Deep levels in II-VI semiconductors

These materials have been, to a large extent, abandoned as potentially important electronic materials because of the "self-compensation" problem which makes it difficult to produce p-n junctions in them. One method to dope these materials p-type is to put shallow acceptors on the Column VI site, but most of the candidates for producing shallow acceptor levels (Column V defects) produce deep levels rather than shallow levels. A notable exception is N, which we predict to yield a shallow acceptor [143][144]. Recent experiments by Bhargava, Merz, and co-workers appear to confirm this. This is a step toward forming p-type II-VI's, but is not the complete solution of the problem because of the effects of Column I impurities on Column II sites — these defects and other aspects of the self-compensation problem require more study.

### I. $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

We have predicted the major chemical trends with alloy composition  $x$  for the deep levels in these technologically important alloys [119].

### J. IV-VI semiconductors

We have developed a theory of the defect levels in these technologically important alloys. We have proposed that the defects In, Ga, and Al are normally found on the anti (Column VI) site, but that Tl is found on the Column IV site in materials such as PbTe. We have been able to explain numerous data including anomalous Hall coefficient and transport measurements, and the pinning of the Fermi level by defects. The "deep resonances" of the Hjalmarson et al. theory [75] are especially important in this regard. One of the most interesting predictions of the theory concerns Cd in PbTe, which is predicted to be a donor at small concentrations but an acceptor at high concentrations.

### K. Paired substitutional defects

Recently we have extended the Hjalmarson et al. theory to pairs of defects [85][87][98][121]. The results of the paired-defect theory are gratifying, especially when one realizes that the input to the theory is only a table of atomic energies plus the band structure of the host.

To date, the data for paired defects that we have studied most thoroughly are the nitrogen-nitrogen and oxygen-defect pairs in  $\text{GaAs}_{1-x}\text{P}_x$  (because Woford, Streetman, and Hess provided data in collaborative interactions). Some successes of the theory for nearest-neighbor pairs in  $\text{GaAs}_{1-x}\text{P}_x$  are: (i) It predicts which pairs of defects are likely to produce deep impurity levels, and which are likely to produce only shallow levels; (ii) It establishes guidelines for selecting a spectator impurity which, when paired with an isolated participant impurity, is likely to manipulate the participant's energy level in a predictable manner; for example, either driving a deep participant level to a shallow pair level or altering a shallow isolated-impurity level to a deep pair state; (iii) It explains why in  $\text{GaAs}_{1-x}\text{P}_x$  the energies  $E$  of deep levels associated with pairs have derivatives

$dE/dx$  which are nearly constant, nearly independent of the defect pair, but somewhat different from the corresponding isolated deep level derivatives; (iv) It predicts the symmetries of deep impurity states; and (v) It answers numerous questions concerning the chemical trends in the paired defect data. For example, the theory explains why the (Ga-vacancy,oxygen) pair lies above the 0 deep level and not below; why electropositive spectator defects such as Zn, Cd, and Mg produce levels when paired with O that all lie at about the same energy, in contrast with electronegative spectators such as Si which produce much deeper pair levels; why paired impurities, each with a deep level, sometimes apparently produce only one deep pair state, not two; and why (Ga-vacancy,donor) pairs produce "deep" luminescence of energy near 1.2 eV in GaAs (namely, the transition are conduction-band to acceptor transition, not donor to valence-band transitions).

The simple theory explains the trends in energies of the (Zn,O) and (Ga-vacancy,O) pairs in  $\text{GaAs}_{1-x}\text{P}_x$ . The (Ga-vacancy,O), (Mg,O), (Zn,O), (Cd,O), and (Si,O) pairs in GaP are compared with theory in Fig. 4. In Fig. 5 we show the predictions for all  $sp^3$ -bonded (X,X) nearest-neighbor pair states in Si. One interesting result is that near-neighbor (P,P) and (As,As) pairs are predicted to form a deep level in Si, but that (Sb,Sb) pairs should not produce a deep impurity state. The As prediction appears to agree with the preliminary ion-implantation data obtained by a student of Karl Hess. Thus Si under very high doping conditions may be better doped with Sb than with P or As.

The qualitative aspects of the pair problem can be understood using a simple symmetry analysis. (The quantitative aspects of the problem are much more difficult: one must predict a level with an accuracy of approximately 0.1 eV, within a  $\approx 1$  eV bandgap, when the controlling physics occurs on a scale of 10 to 20 eV.) By studying the qualitative aspects of the theory and how they relate to the major chemical trends, we have been able to construct a general theory which, if somewhat imprecise, nevertheless can predict trends, can give decent estimates of the changes to be expected in deep trap energies as the host or defect is changed, and can be adjusted systematically to predict other trap energies semi-empirically rather quantitatively — once a few trap levels for a single host are determined. For example, in the case of paired substitutional defects in zincblende hosts, the qualitative nature of the deep level spectrum is dictated by symmetry.

For  $sp^3$ -bonded point defects in tetrahedral ( $T_d$ ) semiconductors, neglecting spin, one can expect a non-degenerate  $A_1$  (s-like) level and a triply degenerate  $T_2$  (p-like) level within or near the bandgap. For nearest-neighbor paired defects, the symmetry is reduced to "molecular" $_{3v}$  (a

levels are a non-degenerate  $a_1$  ( $\sigma$ -like) and a doubly degenerate  $e$  ( $\pi$ -like). The  $e$  levels originate from the  $T_2$  point defect states, and correspond to  $\pi$ -like molecular orbitals polarized perpendicular to the molecular axis. These  $\pi$ -like orbitals do not overlap very much and so the  $e$  molecular states have energies 2 levels. The  $a_1$  molecular

Hence symmetry implies that deep  $T_2$  levels associated with point defects will be split by pairing with a spectator into a doubly degenerate  $e$  level and a singly degenerate  $a_1$  level; the  $e$  level, being only weakly affected by pairing, is likely to remain a deep trap, but the  $a_1$  level can be driven from the gap by a suitable spectator impurity. Likewise,  $A_1$ -symmetric point defect levels form  $a_1$  molecular levels and are susceptible to manipulation by pairing

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 L. Technological significance of the theory of  
paired and clustered defects.

Deep impurity levels often limit the efficiency of electronic or opto-electronic devices by trapping carriers or excitons. For example, some deep levels are efficient non-radiative recombination centers which trap excitons and degrade their energy into heat (phonons) reducing the luminescent yield of light emitters. In many cases, it is economically impractical to remove the defect responsible for the deep level, but practical to add a second "spectator" impurity to the material; the spectator can be chosen so that it will pair with the bothersome defect, either driving the deep level out of the bandgap (so that the deep level no longer traps) or altering the deep defect's energy and configuration coordinates so that non-radiative recombination becomes improbable. The theory of paired defects prescribes the spectator impurities most likely to be successful spectators when paired with a particular bothersome defect.

Ultra-small electronic devices will necessarily be heavily doped in order to limit the interactions among devices. As a result, pairs and clusters of impurities will be much more probable than in current lightly doped devices. The prediction that pairs of shallow donors can produce a deep level is especially disturbing for such small devices. Most notably, we find that nearest-neighbor P pairs in Si produce a deep level [121].

$\downarrow$   
 M. Defects at interfaces.

We have evaluated the effects of interfaces on deep levels for over 100 different semiconductor/semiconductor interfaces. It is widely, but incorrectly, assumed that impurities at interfaces will behave the same as impurities in the bulk. This is not the case in general. We have shown, for example, that P on a Si site at a Si/GaP interface should produce a deep level in the gap rather than the shallow effective-mass level expected of this common dopant (Fig. 6). For weak interfaces, such as  $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$ , the effects of the interface on defect levels are relatively unspectacular, but in a few cases the difference is spectacular — and bothersome.

$\downarrow$   
 N. Defects at surfaces and Schottky barrier heights.

We have evaluated the effects of lattice-relaxed surfaces on deep levels and have used these results to interpret observed Schottky barrier heights in terms of Fermi-level pinning. In the Fermi-level pinning model of Bardeen for heavily n-doped semiconductors, the Fermi level of the surface, defined as the lowest surface level that can accommodate an extra electron, aligns with the Fermi levels of the bulk n-type semiconductor and the metal. This alignment is



achieved by the diffusion of charge, which results in band bending and a Schottky barrier height approximately equal to the energy of the conduction band minimum relative to the lowest unfilled surface level. As suggested by Spicer and co-workers, the surface level responsible for Fermi-level pinning is a native defect level. Our calculations have shown that antisite defects at the semiconductor surface can account for the observed Schottky barrier heights (Fig. 7) — a viewpoint that is gaining widespread experimental support. Furthermore the controversy between Spicer and Brillson concerning the importance of chemical reactivity of the metal in determining Schottky barrier heights in InP and other materials appears to be largely resolved by the hypothesis that different metals (as well as different surface treatments) produce different dominant Fermi-level pinning defects (Fig. 8) — indicating that both major schools of thought are correct. Thus the theory accounts for (i) the alloy dependence of Schottky barrier heights in  $\text{In}_{1-x}\text{Ga}_x\text{As}$  and  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , Fig. 7, and (ii) the dependences of Schottky barrier heights on metal reactivity (Fig. 8).

While the Fermi-level pinning model of Schottky barrier formation is becoming generally accepted for III-V semiconductors, the Schottky barriers formed by Si, most notably with transition-metal silicides, have remained a mystery until very recently [156]. We now have an explanation of these barrier heights based on Fermi-level pinning by Si dangling bonds at the Si/transition-metal silicide interfaces [156]; the theory accounts for the major experimental facts, while unifying the understanding of Si Schottky barriers with that of III-V barriers.

Our theoretical guidelines can now be used to tailor Schottky barriers (or to make ohmic contacts) by deliberately manipulating the defect composition of a semiconductor surface.

#### 0. Intrinsic surface state

We have predicted the energy band structures of surface states at the relaxed (110) surfaces of all the III-V semiconductors [122][126][128][131], at the (100)  $2\times 1$  asymmetric dimer surface of Si [139], and the Si (111) surface (with the buckled geometry) [130]. Our results include tracking resonances throughout the surface Brillouin zone (which has not been done so thoroughly before) and reestablishing the asymmetric dimer model of the Si (100)  $2\times 1$  surface by demonstrating that this model describes the photoemission data well. (This feat is presently beyond the capabilities of self-consistent pseudopotential calculations.) Typical results, for InP, are given in Fig. 9.

#### P. Intrinsic interface states

We have predicted the intrinsic interface states for over 100 semiconductor/semiconductor interfaces. We have speculated about the role of antisite and other defects in the formation of heterojunctions [142][149]. We have shown that interface states have similar physics to deep levels associated with extended defects, and that some interface states have energies that are insensitive to the valence band edge discontinuity at the interface [136].

Our studies of GaAs/oxide interfaces led us to conclude that oxygen can act as both a shallow donor and a shallow acceptor at the interface — although it is a deep trap in bulk GaAs. This conclusion explained several anomalies in the data [129].

#### Q. Core excitons

We have exploited the similarity between the spectra of impurities with an extra positive nuclear charge and the spectra of core excitons (which correspond to "impurities" with an extra positive localized hole) to predict a new kind of antibonding Frenkel core exciton [77][145]. We have evaluated the effects of interfaces [81] and surfaces [88][112] on such core excitons, and have accounted for a large body of formerly puzzling data (Fig. 10).

We have predicted the dependences of the Si 2p core exciton energy on the alloy composition  $x$  in  $\text{Si}_x\text{Ge}_{1-x}$  alloys — and have predicted that for  $x=0.2$  the exciton switches from being a resonance to being a bound state [137]. This dramatic prediction has recently been confirmed by preliminary experiments of Bunker et al.

#### R. Disordered systems

We have predicted the chemical trends for deep levels in  $\text{SiO}_2$  [141] and in amorphous Si [89].

We have studied alloy broadening of spectral lines [90][111] and investigated the effects of Anderson disorder in two [101] and three [125] dimensions. We have studied the effects of alloy disorder on phonons in III-V alloys, both in a one-dimensional model [86] and in a realistic model.

#### S. Thermal conductivity of superlattices

We have evaluated the thermal conductivity of a model superlattice and have shown that mini-umklapp processes can increase the thermal resistance by a factor of typically less than three.

#### T. Metastable semiconductors

We have proposed a theory of a new kind of order-disorder zincblende-diamond phase transition in metastable  $(\text{III-V})_{1-x}(\text{IV})_{2x}$  alloys and have shown how the phase transition affects the band edges [147][151], deep levels [155], surface states [150], interface states, and phonon spectra of such alloys. Recent x-ray diffraction data by J. Greene et al. confirm the predicted zincblende-diamond transition in  $(\text{GaSb})_{1-x}\text{Ge}_{2x}$  (Fig. 11).

An especially notable feature of this new approach is that we have separated the phase transition part of the problem from the problem of evaluating the electronic and vibrational excitations: A phenomenological spin Hamiltonian is constructed for treating the total energy and order parameter of the alloy. This order parameter specifies the probability of finding, say, a Group III atom on a nominal Group V site; and this probability is used to determine a generalized virtual crystal Hamiltonian for electronic structure

Cont'd

and to determine the recursion method solution for the vibrational states of the alloy.

If the separation of this alloy problem carries over to more general problems, it will be possible to use our approach for calculating many different types of phase transitions in semiconductors. Some possibilities: (i) studies of polytypes of SiC, (ii) zincblende-wurtzite phase transitions, (iii) metastable interfacial phases, and (iv) metastable superlattices.

#### U. Technological importance of metastable semiconductors

With new crystal-growth possibilities, as exemplified by the growth of  $(\text{GaAs})_{1-x}\text{Ge}_x$  by ion bombarding a growing film, entirely new classes of metastable but long-lived materials will be fabricated. These materials will have novel electronic properties and some of them may be technologically important. For example, we have already predicted that metastable  $(\text{InP})_{1-x}\text{Ge}_x$  should have a band gap comparable with that of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  (near  $0.1\mu\text{m}$ ). If this material can be made electronics-grade, it could possibly supplant  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  as an infrared detector material.

#### V. Disordered superlattices

We have shown how superlattices can be deliberately disordered and we have predicted how specific disorder produces interesting densities of states [105].

#### W. Phonons in III-V alloys

We have executed a large number of recursion-method calculations of the local densities of phonon states of III-V alloys. These calculations explain the main features of Raman and infrared data.

#### X. Deep levels in superlattices

We have developed the first comprehensive theory of deep levels in superlattices. We have shown that impurities which produce only shallow levels in the fundamental band gap of a bulk semiconductor can become deep levels in superlattices as the thickness of one type of layer decreases. This happens even though the superlattice has the same average composition as the bulk semiconductor; yet in one material the impurity produces a deep level in the gap, while in the other it does not. We have shown that common dopants, e.g., Si in  $\text{GaAs}/\text{Al}_x\text{Ga}_{1-x}\text{As}$  superlattices, exhibit this shallow-deep transition — which has serious implications for doped superlattices.

We have proposed schemes for circumventing this problem, and have elucidated the dependence of deep impurity levels on the impurity's proximity to an interface of the superlattice and on the reduced point-group symmetry of the defect.

Publications of J. D. Dow

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## Figure Captions

Fig. 1. Densities of phonon states (top) and phonon dispersion curves (bottom) for GaSb. The density of states obtained by the recursion method (solid line) is compared with the one obtained by the Lehmann-Taut method (dashed line). The phonon dispersion curves are obtained using the force-constant parameters for GaAs from Table I (solid lines), and are compared with the infrared reflection data from Ref. [23] at  $\Gamma$  point (circles), and with the neutron scattering data from Ref. [24] (dotted lines). The energies of various phonons are denoted on the density of states figure, as, for example, LO:U,K for the LO phonon at the U and K points of the Brillouin zone. The symmetry points of the Brillouin zone are  $\Gamma=(0,0,0)$ ,  $L=(2\pi/a_L)(1/2,1/2,1/2)$ ,  $X=(2\pi/a_L)(1,0,0)$ ,  $U=(2\pi/a_L)(1,1/4,1/4)$ , and  $K=(2\pi/a_L)(3/4,3/4,0)$ .

Fig. 2. Densities of phonon states (top) and phonon dispersion curves (bottom) for Ge. The density of states obtained by the recursion method (solid line) is compared with the one obtained by the Lehmann-Taut method (dashed line). The phonon dispersion curves are obtained in the present model (solid lines), and are compared with the neutron scattering data from Ref. [25] (dotted lines).

Fig. 3. Densities of phonon states for  $(\text{GaSb})_{1-x}\text{Ge}_{2x}$  alloys obtained by the recursion method in the case of  $M = 1 - x$  (solid lines), along with density of states obtained using the persistent approximation for  $x = 0.5$  (dashed line). The assignments given to prominent peaks represent bonds that are responsible for the vibrations giving rise to the peaks (see text).

Fig. 4. Densities of phonon states for  $(\text{GaSb})_{1-x}\text{Ge}_{2x}$  alloys obtained by the recursion method in the case of  $M$  determined by mean-field theory (solid lines), along with density of states obtained using the persistent approximation, Eq. (2.19), for  $x = 0.5$  (dashed line). The assignments given to prominent peaks represent bonds that are responsible for the vibrations giving rise to the peaks (see text).

Fig. 5. (a) Raman spectrum for  $(\text{GaSb})_{0.87}\text{Ge}_{2(0.13)}$  from Refs. [6] and [7]; (b) calculated density of phonon states for the same alloy obtained by the recursion method in the case of  $M$  determined by mean-field theory; and (c) calculated density of states in the case of  $M = 1 - x$ .

Fig. 6. (a) Raman spectrum for  $(\text{GaSb})_{0.76}\text{Ge}_{2(0.24)}$  from Refs. [6] and [7]; (b) calculated density of phonon states for the same alloy obtained by the recursion method in the case of  $M$  determined by mean-field theory; and (c) calculated density of states in the case of  $M = 1 - x$ .

Fig. 7. (a) Raman spectrum for  $(\text{GaSb})_{0.66}\text{Ge}_{2(0.34)}$  from Refs. [6] and [7]; (b) calculated density of phonon states for the same alloy obtained by the recursion method in the case of  $M$  determined by mean-field theory; and (c) calculated density of states in the case of  $M = 1 - x$ .

Fig. 8. (a) Raman spectrum for  $(\text{GaSb})_{0.44}\text{Ge}_{2(0.56)}$  from Refs. [6] and [7]; (b) calculated density of phonon states for the same alloy obtained by the recursion method in the case of  $M$  determined by mean-field theory; and (c) calculated density of states in the case of  $M = 1 - x$ .

Fig. 9. (a) Raman spectrum for  $(\text{GaSb})_{0.20}\text{Ge}_{2(0.80)}$  from Refs. [6] and [7]; (b) calculated density of phonon states for the same alloy obtained by the recursion method in the case of  $M$  determined by mean-field theory; and (c) calculated density of states in the case of  $M = 1 - x$ .

Fig. 10. (a) Total line width in  $\text{cm}^{-1}$  as a function of composition  $x$  for the GaSb-like (triangles) and Ge-like (circles) LO modes, after Ref. [7]. The GaSb-like mode has been fit [7] to two straight lines (dashed curve). The entropy  $S$  per site (divided by Boltzmann's constant) as a function of  $x$ , calculated using mean-field theory for  $(\text{GaSb})_{1-x}\text{Ge}_{2x}$  and assuming  $x_c = 0.3$  (solid curve) is plotted on the scale on the right-hand side of the figure. The scales have been chosen such that the Ge LO mode linewidth and  $S(x)/k_B$  coincide at their maxima. (b) Entropy  $S$  per site as a function of  $x$ , calculated using the on-site model of Eq. (2.11) (solid line) and the phase-transition model with  $x_c = 0.2$  (dashed line) and  $0.7$  (dotted line). Note (in part a) the similar shapes of  $S(x)$  and the line width of the Ge-like LO mode. Note also the kink discontinuities in  $S(x)$  at  $x_c$  (characteristic of a phase transition) that are seen both in the theory and in the experimental line-width curves at  $x = 0.3$  to  $0.4$ . The maximum of  $S(x)$  would not necessarily occur at  $x = 0.3$  if the critical composition were different (part b). For  $x_c < 1/3$  the discontinuity in  $S$  occurs at  $x_c$  and the maximum occurs at  $x = 1/3$ , as demonstrated for  $x_c = 0.2$  (dashed line of part b); for  $x_c > 1/3$ , the maximum occurs at  $x = x_c$ , as demonstrated for  $x_c = 0.7$  (dotted line of part b).

Fig. 11. Illustrating our interpretation of the discontinuity as a function of  $x$  in the Raman peak position of the Ge-like LO mode, as observed in Ref. [7]: There are two principal bond vibrations, Ge-Ge and Ga-Ge. We have drawn parallel lines through the data for Ge-Ge and Ge-Ga modes, separated by  $\approx 7\text{cm}^{-1}$ , the separation predicted for  $x = 0.8$ . Note that the theory, which does not include long-ranged forces, does not accurately predict the positions or slopes of these lines, but only predicts the splitting between them.

Fig. 12. Raman peak positions  $\Omega$  (in  $\text{cm}^{-1}$ ) of the GaSb  $\vec{k}=\vec{0}$  LO and TO modes in  $(\text{GaSb})_{1-x}\text{Ge}_{2x}$  versus alloy composition  $x$ , after Ref. [7], compared with the predictions of the phase-transition model plus a Lyddane-Sachs-Teller LO-TO splitting proportional to the square of the order parameter  $M$ . The bifurcation at  $x_c = 0.3$  of the diamond-phase optic mode (O) into LO and TO modes is characteristic of the order-disorder zincblende-diamond phase transition. Here the theory is shifted down  $\approx 4\text{cm}^{-1}$  to coincide with the data for GaSb, but the variation of the peak position with  $x$ ,  $d\Omega/dx$ , is not adjusted to account for long-ranged forces omitted from the model, and so is not accurately predicted.

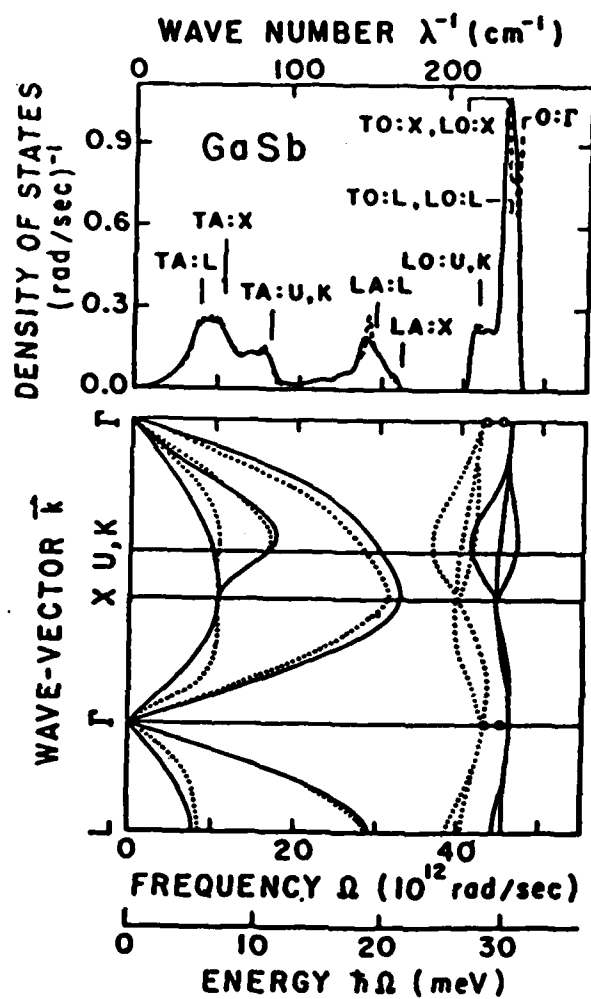


Figure 1

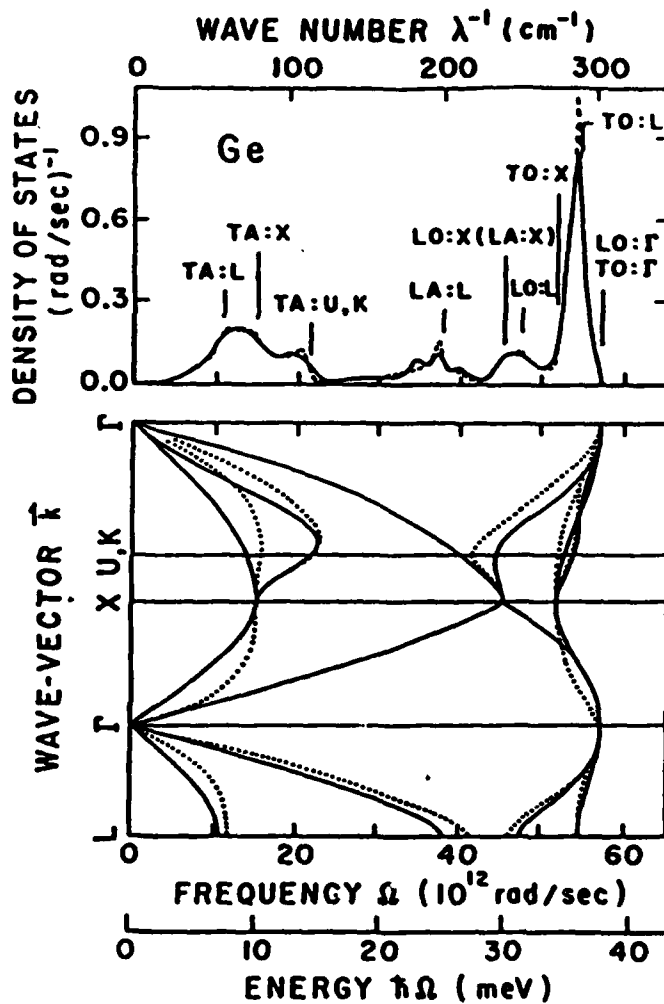


Figure 2

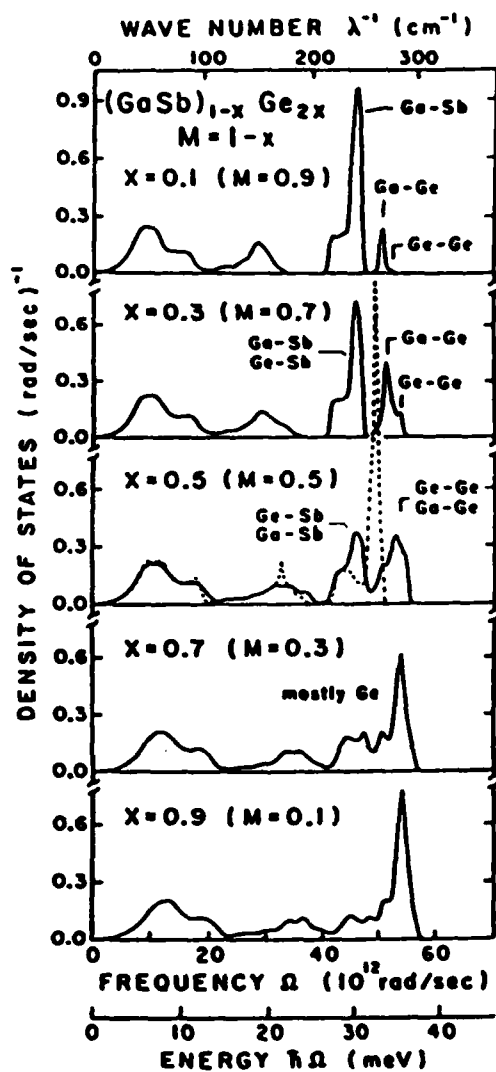


Figure 3

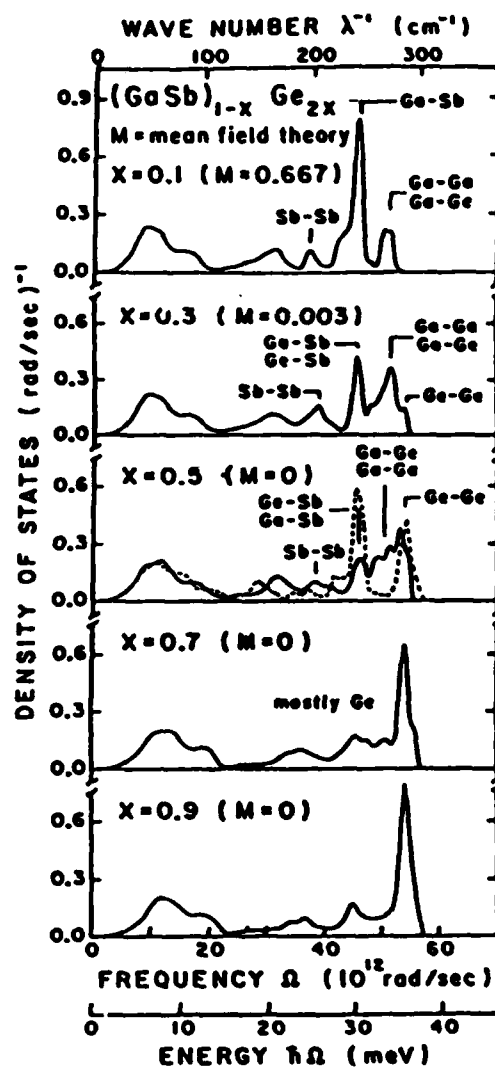


Figure 4

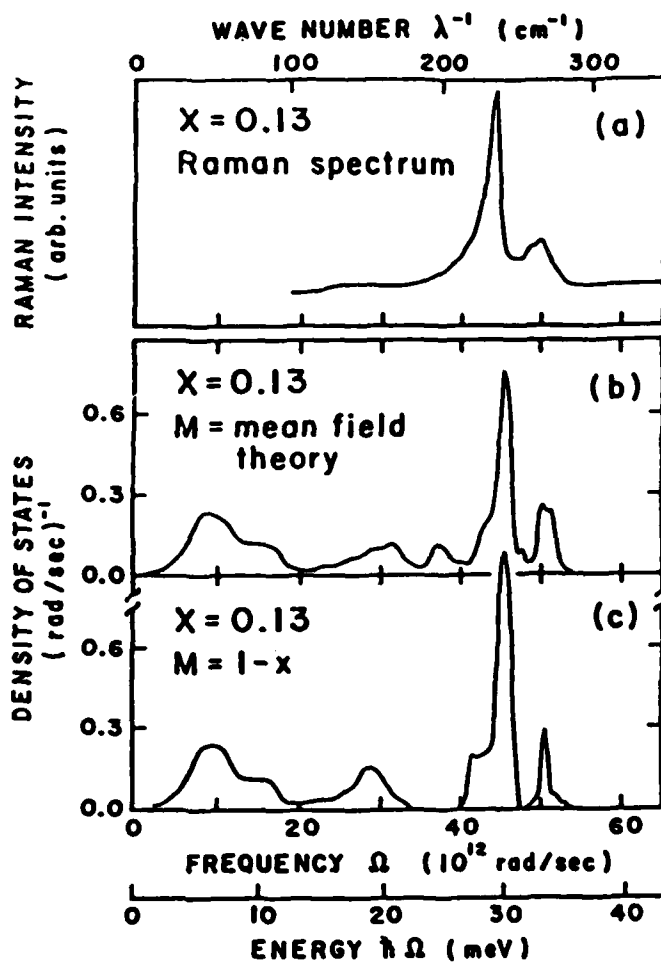


Figure 5

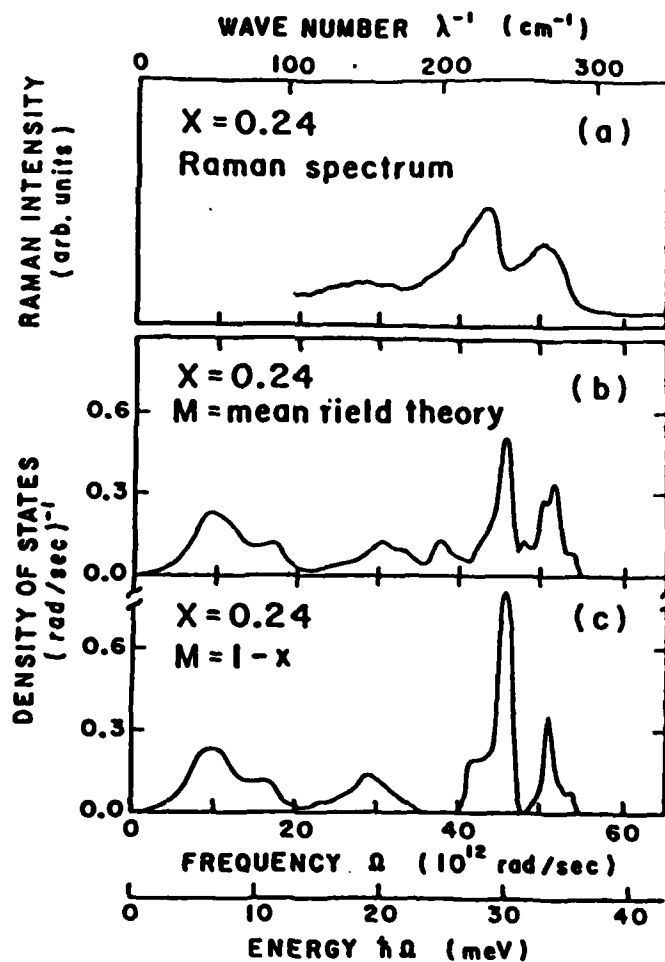


Figure 6



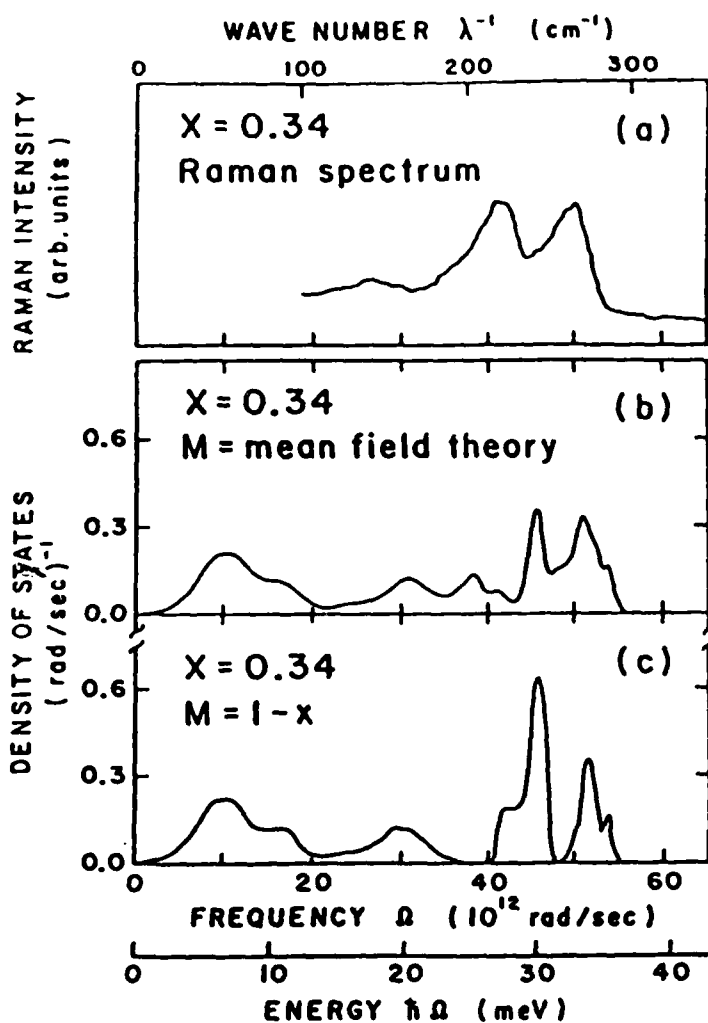


Figure 7

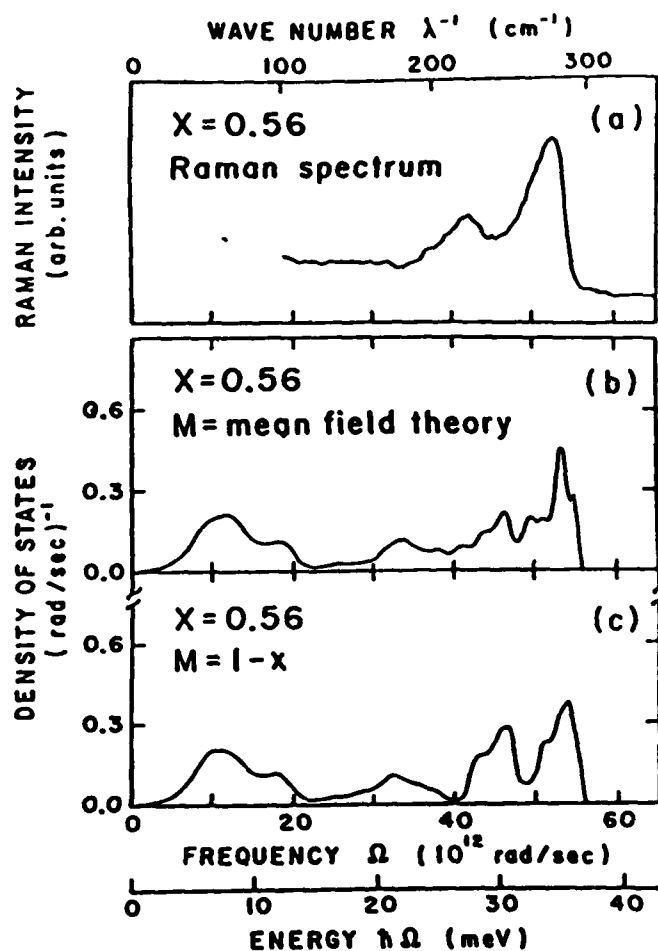


Figure 8

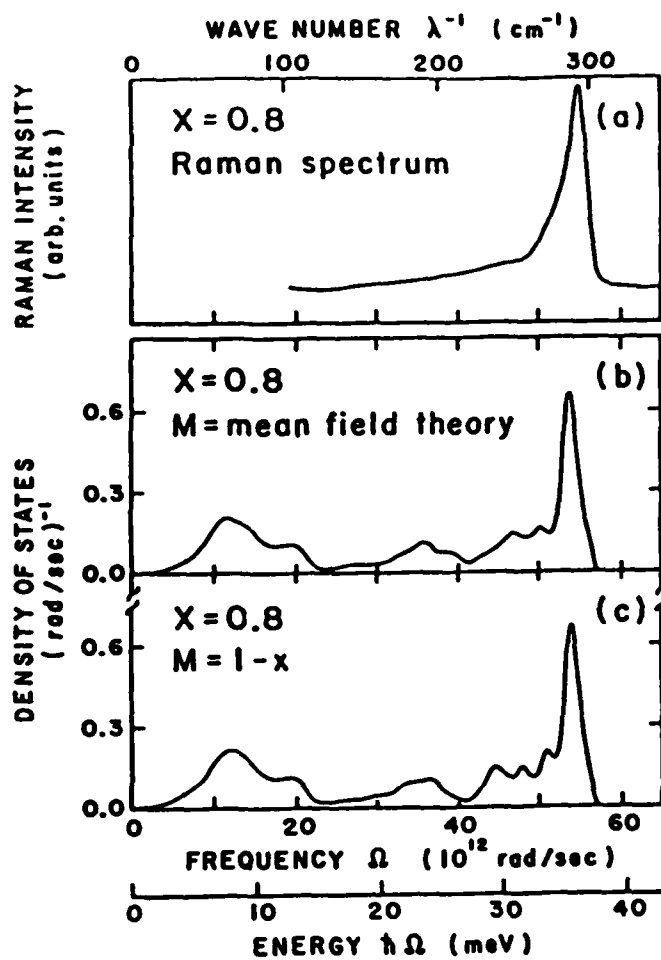


Figure 9

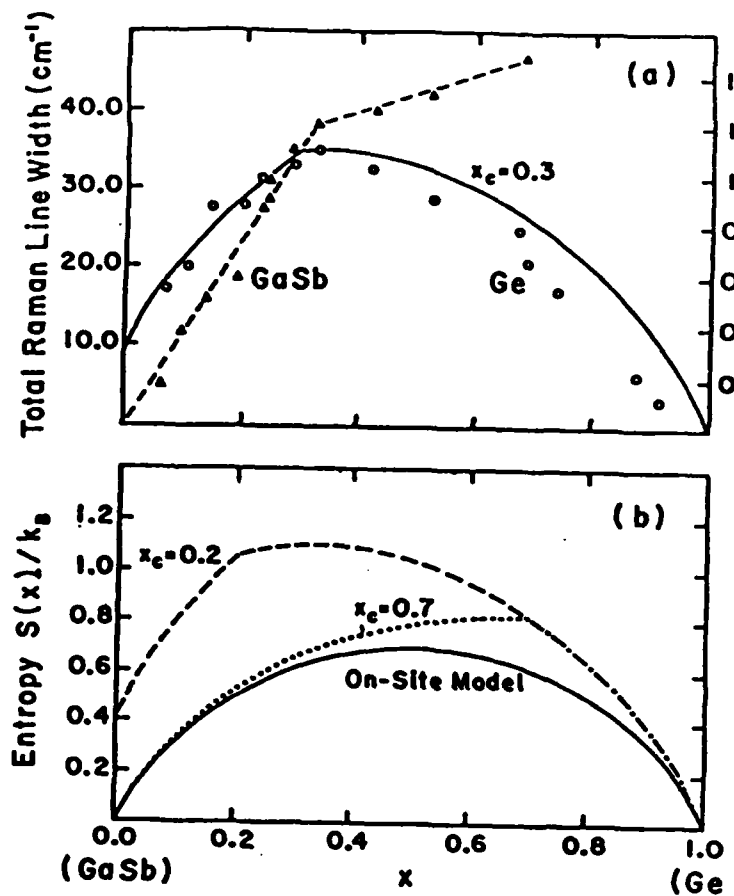


Figure 10

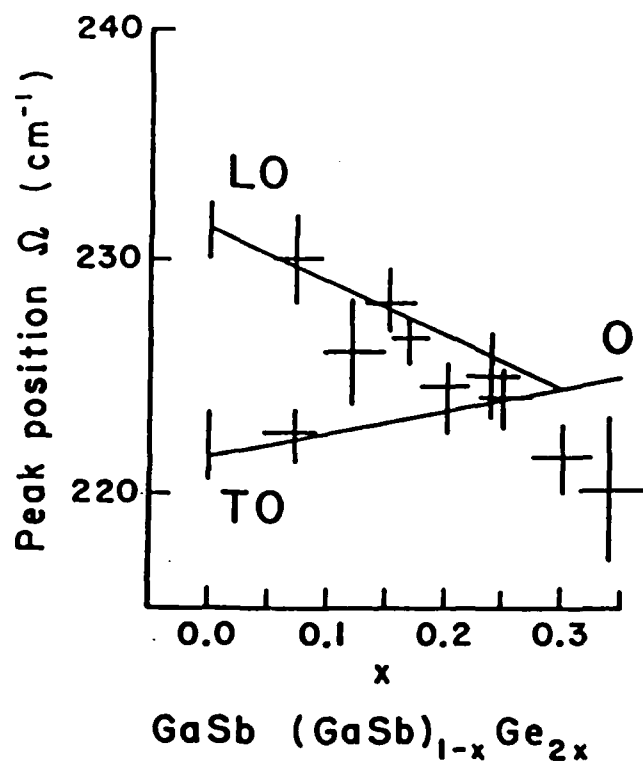


Figure 11

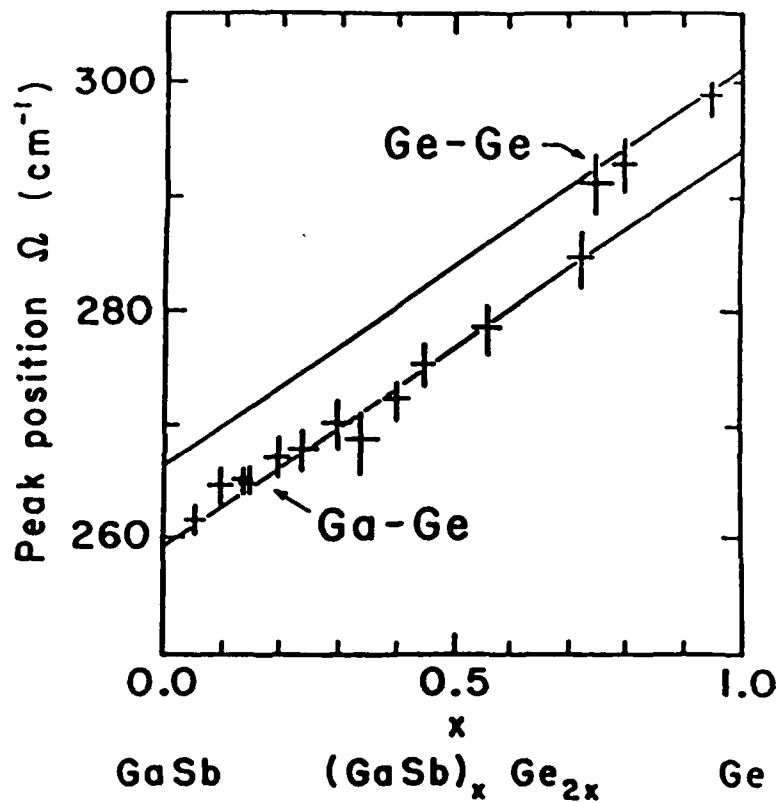


Figure 12

**END**

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